Claims:

1. A method of analyzing a substance, the method comprising:

(1) ionizing the substance to form a stream of ions;

(2) subjecting the ion stream to a first mass analysis, to select ions having a desired mass to charge ratio, as precursor ions;

(3) introducing the precursor ions into a collision cell to promote fragmentation of the precursor ions, thereby to generate primary fragment ions;

(4) in the collision cell, selecting primary fragment ions having a desired mass to charge ratio, and rejecting other ions;

(5) accelerating the selected primary fragment ions from the collision cell into a downstream mass analyzer, thereby to promote secondary fragmentation; and

(6) mass analyzing the secondary fragment ions to generate a mass spectrum.

2. A method as claimed in claim 1, wherein step (3) comprises accelerating the precursor ions into the collision cell, to promote fragmentation by collision with the gas.

3. A method as claimed in claim 1 or 2, wherein selection of the primary fragment ions in step (4) comprises removing ions of a mass to charge ratio greater than the mass to charge ratio of the selected primary fragment ions and separately removing ions with a mass to charge ratio less than the mass to charge ratio of the selected primary fragment ion, the removal of the ions with mass to charge ratios higher and lower than the mass to charge ratio of the selected primary fragment ion being effected in either order.

4. A method as claimed in claim 3, which includes effecting removal of primary fragment ions with mass to charge ratios greater and less

than the mass to charge ratio of the selected primary fragment ion in the collision cell.

5. A method as claimed in claim 4, which includes trapping the primary fragment ions and any residual precursor ions in the collision cell, during step (4).

6. A method as claimed in any preceding claim, which includes effecting step (6) by scanning ions out of the downstream mass analyzer by an axial ejection technique in a linear ion trap mass spectrometer.

7. A method as claimed in any one of claims 1 to 5, which includes effecting step (6) by passing the ions into a time-of-flight instrument for mass analysis.

8. A method of analyzing a substance, the method comprising:

(1) ionizing the substance to form a stream of ions;

(2) subjecting the ion stream to a first mass analysis, to select ions having a desired mass to charge ratio, as precursor ions;

(3) introducing the precursor ions into a collision cell to promote fragmentation of the precursor ions, thereby to generate primary fragment ions;

(4) in the collision cell, selecting primary fragment ions having a desired mass to charge ratio, and rejecting other ions by removing ions of a mass to charge ratio greater than the mass to charge ratio of the selected primary fragment ions and separately removing ions with a mass to charge ratio less than the mass to charge ratio of the selected primary fragment ion, the removal of the ions with mass to charge ratios higher and lower than the mass to charge ratio of the selected primary fragment ion being effected in either order;

(5) causing the selected primary fragment ions to collide, to promote further fragmentation, generating secondary fragment ions; and

(6) mass analyzing the secondary fragment ions to generate a mass spectrum.

9. A method as claimed in claim 8, wherein step (3) comprises accelerating the precursor ions into a collision cell, to promote fragmentation by collision with the gas.

10. A method as claimed in claim 8 or 9, which includes trapping the primary fragment ions and any residual precursor ions in the collision cell, during step (4).

11. A method as claimed in claim 8 or 9, which includes effecting step (5) by accelerating ions from the collision cell into a downstream mass analyzer, thereby to promote secondary fragmentation.

12. A method as claimed in claim 11, which includes effecting step (6) by scanning ions out of the downstream mass analyzer by an axial ejection technique.

13. A method as claimed in claim 11, which includes effecting step (6) by passing the ions into a time-of-flight instrument for mass analysis.

14. A method as claimed in claim 8, which includes sequentially repeating steps (4) and (5) to effect multiple mass analysis cycle, wherein, for each cycle, step (4) comprises selecting further fragment ions from fragment ions generated by a previous fragmentation step and rejecting ions with a differing mass to charge ratio, and step (5) comprises causing said further fragment ions to collide, to promote further fragmentation, generating another generation of fragment ions.

15. A method of analyzing a substance, the method comprising:

(1) ionizing the substance to form a stream of ions;

(2) subjecting the ion stream to a first mass analysis, to select ions having a desired mass to charge ratio, as precursor ions;

(3) accelerating the precursor ions together with a collision gas into a low pressure section, to promote fragmentation of the precursor ions, thereby to generate primary fragment ions; and

(4) subjecting the fragment ions to a second mass analysis, to generate a mass spectrum.

16. A method as claimed in claim 15, wherein (3) includes providing a multipole rod set in the low pressure section, for at least promoting collection and focusing of ions received therein, and providing at least an RF voltage to the multipole rod set to focus ions.

17. A method as claimed in claim 16, which includes providing a quadrupole rod set as the multipole rod set, and setting the q value of the quadrupole rod set to provide a high fill mass that is approximately 1/2 that of the mass to charge ratio of a desired ion.

18. A method as claimed in claim 15, which includes effecting step (4) in a time of flight mass analyzer.

19. A method as claimed in claim 16, which includes passing ions through the multipole rod set into a time of flight mass analyzer and mass analyzing the ions in the time of flight mass analyzer, to effect step (4).

20. A method as claimed in claim 16 or 17, which includes trapping the ions in the multipole rod set, and scanning ions out axially from the multipole rod set to effect the second mass analysis of step (4).

21. A method as claimed in claim 16, which includes providing the RF voltage during the fill step such that the q value of the low m/z ions is greater than q=0.9, to at least delay capture by the multipole rod set of ions with a low mass to charge ratio.

22. A method as claimed in claim 21, which includes setting the RF level to enhance sensitivity for ions of a desired mass to charge ratio.

23. A method as claimed in claim 21, which includes: providing the elevated RF level as a first RF voltage for pre-determined delay time, to cause the primary fragment ions to dissipate energy by collision with the collision gas, and then lowering the RF level to a second, lower RF voltage whereby lower m/z ions can be trapped.

24. A method as claimed in claim 23, which includes setting the delay time to reduce the energy of the primary fragment ions to a level sufficient to substantially suppress formation of secondary fragment ions, and subsequently reducing the RF level to the second, lower RF voltage for the second mass analysis of step (4).

25. A method as claimed in claim 21, 22, 23 or 24, which includes trapping ions in the multipole rod set and scanning ions out to effect the second mass analysis of step (4).

26. A method as claimed in claim 25, which includes progressively increasing at least one of a RF voltage and an AC voltage applied to the multipole rod set, to scan ions out of the multipole rod set by axial ejection.

27. A method as claimed in claim 25, which includes, after reducing the RF voltage to the second RF voltage, providing a cool time period, to enable any excess energy of the ions to dissipate by collision before effecting the second mass analysis of step (4), and effecting the second mass analysis by scanning ions out from the multipole rod set.